(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 799 900 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
08.10.1997 Bulletin 1997/41

(51) Int. Cl.^{6}: C22C 21/06, C22C 21/10

(21) Application number: 96200967.6

(22) Date of filing: 04.04.1996

(84) Designated Contracting States:
NL

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(54) High strength aluminium-magnesium alloy material for large welded structures

(57) The present invention provides a chemistry window and method to manufacture light weight Al-Mg alloy plate materials having significantly improved strength in both soft and work hardened tempers as compared to those of AA5083. It is claimed that the materials produced according to the present invention have ductility, pitting, stress and exfoliation corrosion resistances equivalent to those of the AA5083. Furthermore, it is claimed that the material of current invention has improved long term stress and exfoliation corrosion resistances at temperatures above 80°C which is the maximum application temperature for the AA5083 alloy. The method comprises of the following manufacturing steps: homogenising an alloy ingot containing 4.5-7 % Mg, 0.4-1.2 % Mn, 0.4-5 % Zn, upto 0.3 % Zr, upto 0.3 % Cr, Ti upto 0.2 %, Fe and Si upto 0.5 %, Cu upto 0.4 %: hot rolling the ingot in the range 400-530°C: cold rolling the plate with or without inter-annealing: final and inter annealing the cold rolled material at temperatures in the range 200-550°C.

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Description

Field of invention

The present invention relates to a composition window and a method of manufacturing light weight, high strength Al-Mg alloy plates to be used in the construction of large welded structures such as storage containers, vessels for marine and land transportations. For example, the plates of this invention can be used in the construction of marine transportation vessels such as catamarans of monohull type, fast ferries, High speed light crafts etc. The alloy plates of the present invention can also be used in numerous other applications such as structural materials for LNG tanks, Silos, tanker lorries and as tooling and moulding plates.

Description of the related art

Al-Mg alloys with Mg levels > 3 % are extensively used in large welded constructions such as storage containers, vessels for land and marine transportations. In particular, the AA5083 alloy plates in the soft and work hardened tempers are used in the construction of marine vessels such as ships, catamarans, high speed crafts. The plates of the AA5083 alloy in the soft temper are used in the construction of tanker lorries, dump trucks etc. The main reason for the versatility of the AA5083 alloy is that it provides the best available combinations of high strength (both at ambient and cryogenic temperatures), light weight, corrosion resistance, bendability, formability and weldability. The strength of the AA5083 alloy can be increased without significant loss in ductility by increasing the Mg % in the alloy. However, increasing the % Mg in Al-Mg alloys is accompanied by a drastic reduction in exfoliation and stress corrosion resistances which may be attributed to the increased extent of precipitation of anodic Mg containing intermetallics on the grain boundaries. Recently, a new alloy 5383 has been introduced with improved properties over AA5083 in both work hardened and soft tempers. In this case, the improvement has been achieved primarily by optimising the existing window of AA5083 alloy.

Summary of the invention

The objective of the present invention is to provide an Al-Mg alloy plate with substantially improved strength in both soft and work hardened tempers as compared to those of the standard AA5083 alloy. It is claimed that alloy plates of the present invention offer ductility, bendability, pitting, stress and exfoliation corrosion resistances equivalent to those of the AA5083. It is also claimed that the welded joints of the present alloy have higher strength than those of the standard AA5083 welds. Furthermore, it is claimed that the material of current invention has improved long term stress and exfoliation corrosion resistances at temperatures above 80°C which is the maximum application temperature for the AA5083 alloy. The above mentioned claims follow the inventions that, higher strength levels in both work hardened and soft tempers can be achieved by increasing the levels of Mg, Mn and Zr, and the stress and exfoliation corrosion resistances at higher Mg levels can be maintained by precipitating relatively less anodic Mg and Zn containing intermetallics within grains. The precipitation of Mg and Zn containing intermetallics within grains effectively reduces the volume fraction of grain boundary precipitated, highly anodic, binary AlMg intermetallics and thereby provides significant improvement in stress and exfoliation corrosion resistances to the alloys of the current invention at higher Mg levels. The new alloy plates can be manufactured by preheating, hot rolling, cold rolling with or without inter-annealing and final annealing of an Al-Mg alloy slab wherein the composition of the ingot contains 4.5-7 % Mg, 0.4-1.2 % Mn, 0.4-5 % Zn, upto 0.3 % Zr, upto 0.3 % Cr, upto 0.2 % Ti, upto 0.5 % Fe, upto 0.5 % Si, upto 0.4 % Cu, the remainders consisting of Al and other inevitable impurities. The conditions are such that a temperature for preheat in the range 400-550°C and a time for homogenisation not more than 24h; the hot rolling preferably begins at 500°C; 20-60 % cold rolling the hot rolled plate with or without interannealing after 20 % reduction; the final and intermediate annealing at temperatures in the range 200-550°C with a heat-up period between 1-10h, soak period at the annealing temperature in the range 10 min to 10 h. The annealing may be carried out after hot rolling step and the final plate may be stretched by a maximum of 6 %.

Detailed description of the preferred embodiments

The reasons for the limitations of the alloying elements and the processing conditions of the aluminium alloy according to the present invention are described herein below:

Chemistry window

Mg : Mg is the primary strengthening element in the alloy. Mg levels below 4.5 % do not provide the required strength and when the addition exceeds 7 %, cracking occurs during hot rolling. The preferred level of Mg is in between 5.2-5.6 %.

Mn : Mn is an essential additive element. In combination with Mg, Mn provides the strength to both plate and the welded joints of the alloy. Mn levels below 0.4 % cannot provide sufficient strength to the alloy. Above 1.2 %, the hot rolling becomes difficult. The preferred range for Mn is 0.7-0.9 %.

Zn : Zn is an important additive for corrosion resistance of the alloy. Zn also contributes to some extent the strength of the alloy in the work-hardened tempers. The preferred range for Zn is 0.4-1.5 %.

Zr : Zr is important to achieving strength improvements in the work hardened tempers of the alloy. Zr is also important for resistance against cracking during welding of the plates of the alloy. Zr levels above 0.3 % results in very coarse needle shaped primary particles which decreases bendability of the alloy plates and therefore the Zr level must be kept below 0.3 %. However to provide sufficient strength in the work hardened tempers a preferred range of 0.10-0.20 % is needed.

Ti : Ti is important as a grain refiner during solidification of both ingots and welded joints produced using the alloy plates of the current invention. However, Ti in combination with Zr form undesirable, coarse primaries. To avoid this, Ti levels must be kept below 0.2 % and the preferred range for Ti is 0.05-0.1 %.

Fe : Fe forms compounds of Al-Fe-Mn during casting, thereby limiting the beneficial effects due to Mn. Fe levels above 0.5 % causes coarse primary particles formation which decrease the fatigue life of the welded joints of the alloy plates of the current invention. The preferred range for Fe is 0.20-0.30 %.

Si : Si forms Mg_2Si which is practically insoluble in Al-Mg alloys containing Mg>4.5 %. Therefore Si limits the beneficial effects of Mg. Si also combines with Fe to form coarse AlFeSi phase particles which can affect the fatigue life of the welded joints of the alloy plate. To avoid the loss in primary strengthening element Mg, the Si level must be kept below 0.5 %. The preferred range for Si is 0.10-0.20 %.

Cr : Cr improves the corrosion resistance of the alloy. However, Cr limits the solubility of Mn and Zr. Therefore, to avoid formation of coarse primaries, the Cr level must be kept below 0.3 %. A preferred range for Cr is 0.1-0.15 %.

Cu : Cu should be kept below 0.4 %. Cu levels above 0.4 % gives rise to unacceptable deterioration in pitting corrosion resistance of the alloy plates of the current invention. The preferred level for Cu is 0.1 %

Preheating and hot rolling

The preheating prior to hot rolling is usually carried out at a temperature in the range 400-530°C in single or in multiple steps. In either case, preheating decreases the segregation of alloying elements in the as-cast material. In multiple steps, Zr, Cr and Mn can be intentionally precipitated to control the microstructure of the hot mill exit material. If the treatment is carried out below 400°C, the resultant homogenisation effect is inadequate. Furthermore, due to substantial increase in deformation resistance of the slab, industrial hot rolling is difficult for temperatures below 400°C. If the temperature is above 530°C, eutectic melting might occur resulting in undesirable pore formation. The preferred time window to perform the above preheat treatment is between 1 and 24 hours. The hot rolling begins preferably at about 500°C. With increase in the Mg % within the window from the preferred Mg %, the initial pass schedule becomes more critical.

Cold rolling and Annealing

A 20-60 % cold rolling reduction is applied to hot rolled plate prior to final annealing. A reduction of 20 % is preferred so that the precipitation of anodic Mg containing intermetallics occurs uniformly during final annealing treatment. Cold rolling reductions in excess of 60 % without any intermediate annealing treatment might cause cracking during rolling. In case of inter-annealing, the treatment is preferably carried out after at least 20 % cold reduction to distribute the Mg and/or Zn containing intermetallics uniformly in the inter-annealed material. Final annealing can be carried out in cycles comprising of single or with multiple steps in either during heat-up and(/or) hold and(/or) cooling down from the annealing temperature. The heat-up period is in between 10 min to 10h. The annealing temperature is in the range between 200-550°C depending upon the temper. The preferred range is in between 225-275°C to produce work hardened tempers and 350-480°C for the soft tempers. The soak period at the annealing temperature in between 15 min to 10h. The cooling rate following annealing soak is preferably in the range 10-100°C/h. The conditions of the intermediate annealing are similar to those of the final annealing.

Example

Table 1 lists the chemistries of the ingots used to produce soft and work hardened temper materials:

Alloy Code	Mg	Mn	Zn	Zr	Ti	Fe	Si	Cr	Cu	Al
A1	4.54	0.64	0.1	0.005	0.02	0.24	0.25	0.1	0.08	Remainders
A2	5.2	0.8	0.2	0.12	0.13	0.25	0.13	< 0.01	0.09	•
A3	4.7	0.8	0.4	0.13	0.14	0.23	0.14	< 0.01	0.1	•
A4	4.7	0.8	0.6	0.13	0.12	0.23	0.13	< 0.01	0.1	•
A5	4.8	0.8	0.2	0.17	0.13	0.23	0.13	< 0.01	0.1	•
A6	4.8	0.8	0.2	0.25	0.13	0.25	0.12	< 0.01	0.1	•
A7	5.9	0.8	0.2	0.23	0.12	0.25	0.13	< 0.01	0.1	•
A8	5.9	0.8	0.6	0.24	0.15	0.24	0.15	< 0.01	0.1	•

Table 1: List of chemistries

The ingots were preheated at a rate of 35°C/h to 510°C. Upon reaching the preheat temperature, the ingots were soaked for a period of 12h prior to hot rolling. The total hot reduction was 95 %. A reduction of 1-2 % was used in the first three passes of hot rolling. Gradually the % hot reduction per pass was increased. The materials exiting the mill had temperature in the range 300± 10°C. A 40 % cold reduction was applied to the hot rolled materials. Soft temper materials were produced by annealing the cold rolled materials at 525°C for a period of 15 min. Work hardened temper materials were produced by soaking the cold rolled materials at 250°C for an hour. The heat-up period was 1h. After the heat treatments, the materials were air-cooled. The tensile properties and corrosion resistances of the resultant materials are listed in table 2. The data of the alloy A1 are the properties of the standard AA5083 alloy. A comparison of the properties listed in table 2 clearly show the significant improvement in tensile strengths without any significant loss either in ductility or in corrosion resistance. Furthermore, it can be noticed from table 2 that the alloys of current invention have more improved strength both in the soft and work hardened tempers as compared to those of AA5383.

Alloy Code	O Temper						H321 Temper				
	Tensile Properties				Corrosion Resistance		Tensile Properties			Corrosion Resistance	
	PS (MPa)	UTS (MPa)	ε_f (%)	n	ASSET test Result	weight Loss (mg/cm²)	PS (MPa)	UTS (MPa)	e_f (%)	ASSET test Result	weight Loss (mg/cm²)
A1	150	295	21.1	0.22	PA	3	285	361	9.8	PA	5
A2	174	327	22.5	0.3	PA	2	326	404	9.7	PA	3
A3	170	323	20.6	0.25	PA	2	329	394	8.8	PA	3
A4	176	332	21.4	0.25	PA	2	331	404	8.4	PA	2
A5	172	328	21.8	0.24	PA	3	326	398	9.8	PA	3
A6	168	322	21.3	0.22	PA	3	350	400	8.7	PA	2
A7	182	344	21.3	0.25	PA	2	331	427	9.7	PA	3
A8	187	356	22.4	0.23	PA	2	347	432	9.6	PA	2
5383	145	290	17				220	305	10		

Table 2: List of tensile and corrosion resistances of the alloys

Claims

1. High strength aluminium magnesium alloy material for large welded structures with the following composition in weight percent:

Mg	4.5 - 7
Mn	0.4 - 1.2
Zn	0.4 - 5
Zr	0.3 max.
Cr	0.3 max.
Ti	0.2 max.
Fe	0.5 max.
Si	0.5 max.
Cu	0.4 max.

remainder Al and inevitable impurities

each	0.05 max.
in total	0.15 max.

- having improved strength in both soft and work hardened tempers as compared to those of AA5083, and at the same time
- having ductility, pitting, stress and exfoliation corrosion resistances equivalent to those of AA5083.

2. The material of claim 1 in which

Mg	5.2 - 5.6
Mn	0.7 - 0.9
Zn	0.4 - 1.5.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0967

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	FR-A-973 802 (TREFILERIES & LAMINOIRS DU HAVRE) ---		
X	"METALS HANDBOOK, VOL 2" 1990 , ASM INTERNATIONAL , OHIO, US XP002011999 *ALLOY 5083* * page 92 - page 93 * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 August 1996	Gregg, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	GB-A-1 458 181 (MITSUBISHI CHEM IND) 8 December 1976 * claim 1 *	1,2	C22C21/06 C22C21/10
X	US-A-2 985 530 (M.C.FETZER ET AL) * claim 1; table 1 *	1,2	
X	GB-A-509 465 (I.G. FARBENINDUSTRIE A.G.) * column 2, line 66 - line 69 *	1,2	
X	FR-A-874 428 (VEREINIGTE LEICHTMETALL-WERKE) * claim 1 *	1,2	
X	CHEMICAL ABSTRACTS, vol. 100, no. 16, 16 April 1984 Columbus, Ohio, US; abstract no. 125388, CAMPBELL, HECTOR S.: "Superior stress corrosion resistance of wrought aluminum-magnesium alloys containing 1% zinc" XP002012000 * abstract * & INST. METALL. [COURSE VOL.], SER. 3 (LONDON) (1983), 20(METALL. LIGHT ALLOYS), 82-100 CODEN: IMCTD6, 1983,	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C
X	US-A-3 171 760 (W.D. VERNAM ET AL) * claim 1 *	1	
A	EP-A-0 462 056 (ALUSUISSE LONZA SERVICES AG) 18 December 1991		
A	DE-A-27 16 799 (SUMITOMO LIGHT METAL IND) 27 October 1977		

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